Mass Spectrometric Investigation of Aliphatic Aldehydes

Th. M. El-Sherbini and S. H. Allam
Physics Department, Faculty of Science, Cairo University, Cairo, Egypt

M. D. Migahed and A. M. Dawoud
Physics Department, Faculty of Science, University of Mansoura, Mansoura, Egypt

Z. Naturforsch. **36a**, 1334—1337 (1981); received September 30, 1981

The mass spectra of C_2 to C_7 *n*-alkanals have been measured using a double focusing mass spectrometer. The various reaction mechanisms by which the fragment ions are formed have been elucidated and discussed. Two reactions, the β-cleavage with rearrangement and the γ-cleavage reactions lead, respectively, to $[C_2H_4O]^+$ and $[C_3H_5O]^+$ ions with significant intensities in butyraldehyde and higher *n*-alkanals.

The electron energy distribution difference (EDD) method together with a computer programme have been used for evaluating ionization efficiency curves for the molecular ions. The ionization potentials obtained by this method show good agreement with those obtained from other electron impact and photoionization experiments.

Introduction

The mass spectra of a large number of aliphatic aldehydes have been previously studied with mass spectrometers by many investigators [1, 2, 3]. Most of these studies have been made with low resolution mass spectrometers, but a few high resolution mass-spectrometric data [4] for these compounds are also available. High resolution mass spectra of these compounds can give more information about the fragmentation reactions and hence a better understanding of the mechanisms of fragmentation can be achieved. Moreover, more accurate ionization potentials for the molecular ions can be obtained.

In this work the mass spectra of C_2 to C_7 *n*-alkanals are obtained with a double focusing mass spectrometer (resolution $\cong 4000$). The relative intensities of the fragment ions are determined and main reaction mechanisms leading to the various fragments are proposed and discussed.

The ionization efficiency (IE) curves are determined using the electron energy distribution difference (EDD) method [5, 6]. The main advantage of this method is to eliminate the effect of the energy spread of the electrons and therefore to obtain true IE curves. This spread in the electron energy, which occurs in conventional electron impact ion sources, obscures many fine structures in the ionization efficiency curves. A least squares-fitting programme was developed in order to fit the data points to straight lines on the ionization efficiency curves and hence to determine accurate ionization potentials for the molecular ions.

Experimental

The mass spectra were recorded with a Varian Mat CH-5-DF mass spectrometer. The resolution was fixed to $M/\Delta M \cong 4000$ during the measurements. The incident electron energy was kept at 30 eV when measuring the mass spectra, while it was varied from 4.5 eV up to 29.5 eV in steps of 0.05 eV for the ionization potential measurements. The ion source operating temperature was about 100 °C. The pressure in the ion source was about 3×10^{-6} torr during the measurements while the background pressure was about 10^{-8} torr. Argon was used as a standard gas for calibrating the electron energy scale when measuring the ionization efficiency curves. Each curve was recorded three times and then the data were averaged.

Results and Discussions

I. Mass Spectra of *n*-alkanals

The mass spectra of the following *n*-alkanals acetaldehyde (C_2H_4O), propionaldehyde (C_3H_6O), butyraldehyde (C_4H_8O), *n*-valeraldehyde ($C_5H_{10}O$), caproaldehyde ($C_6H_{12}O$), enanthaldehyde ($C_7H_{14}O$), were recorded at 30 eV electron energy. The main reaction mechanisms by which the fragment ions

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Reprint requests toDr. Th. M. El-Sherbini, Physics Department, Faculty of Science, Cairo University, Cairo. Egypt.

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appearing in the spectra are formed, can be classified as follows:

1. *α-cleavage*

It occurs as a result of a C-C bond rupture between the carbonyl group and the CHO:

$$C_xH_{2x+1}CHO^+ \rightarrow [C_xH_{2x+1}]^+ + CHO$$

$$\text{or} \quad [CHO]^+ + C_xH_{2x+1} \, .$$

The relative intensities expressed as a percentage of the total ion current, for the alkyl ions and $[CHO]^+$ of the alkanals under study are listed in Table 1. It is clear from the relative intensities of the alkyl and $[CHO]^+$ ions that α-cleavage is an important mechanism for propionaldehyde, acetaldehyde and butyraldehyde, and less important for the higher *n*-alkanals.

2. *β-cleavage*

The relative intensities of the ions formed by the β-cleavage reaction are given in Table 2. It appears from the table that the ions formed by β-cleavage are nearly of equal importance for all the *n*-alkanals.

3. *β-cleavage with Rearrangement (McLafferty rearrangement)*

This rearrangement involves "β-cleavage" in which a hydrogen atom is apparently transferred [7, 8] during the process as illustrated in Figure 1. It is one of the most prominent and commonly-found rearrangements in butyraldehyde and higher *n*-alkanals, which is evident from the relatively large intensities of the resultant ions (see Table 3).

Table 1. Relative intensities of alkyl ions and CHO^+ ions formed by α-cleavage.

Alkanal	Alkyl ion	Intensity (%)	Ion containing oxygen	Intensity (%)
Acetaldehyde (n-C_2)	CH_3	—	CHO	25.4
Propionaldehyde (n-C_3)	C_2H_5	22.5	CHO	7.8
Butyraldehyde (n-C_4)	C_3H_7	12.3	CHO	2.5
N-valeraldehyde (n-C_5)	C_4H_9	0.8	CHO	1.8
Caproaldehyde (n-C_6)	C_5H_{11}	0.4	CHO	0.8
Enanthaldehyde (n-C_7)	C_6H_{13}	0.3	CHO	0.8

Table 2. Relative intensities of alkyl ions and $[C_2H_3O]^+$ formed by β-cleavage.

Alkanal	Alkyl ion	Intensity (%)	Ion containing oxygen	Intensity (%)
Propionaldehyde (n-C_3)	CH_3	—	C_2H_3O	0.4
Butyraldehyde (n-C_4)	C_2H_5	5.4	C_2H_3O	3.0
N-valeraldehyde (n-C_5)	C_3H_7	4.0	C_2H_3O	1.5
Caproaldehyde (n-C_6)	C_4H_9	3.2	C_2H_3O	1.0
Enanthaldehyde (n-C_7)	C_5H_{11}	1.7	C_2H_3O	1.1

4. *γ-cleavage*

The mass spectra of the *n*-alkanals show considerable intensities at $m/e = 57$, which is attributed to $[C_3H_5O]^+$ ions formed by γ-cleavage. This indicates the importance of γ-cleavage in the fragmentation of *n*-alkanals. The relative intensities of $[C_3H_5O]^+$ and alkyl ions formed by the γ-cleavage reaction are given in Table 4.

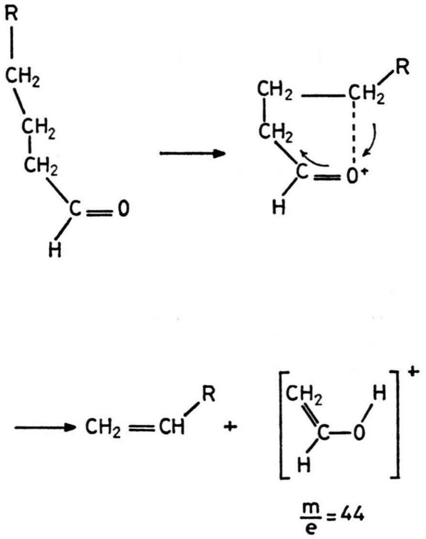

Fig. 1. The β-cleavage with rearrangement (McLafferty rearrangement), where R can be either hydrogen atom "butyraldehyde" or any other radical.

Table 3. Relative intensities of alkyl ions and $[C_2H_4O]^+$ formed by β-cleavage with rearrangement.

Alkanal	Alkyl ion	Intensity (%)	Ion containing oxygen	Intensity (%)
Butyraldehyde (n-C_4)	C_2H_4	—	C_2H_4O	27
N-valeraldehyde (n-C_5)	C_3H_6	3.5	C_2H_4O	36.8
Caproaldehyde (n-C_6)	C_4H_8	20.7	C_2H_4O	22.1
Enanthaldehyde (n-C_7)	C_5H_{10}	15	C_2H_4O	13.1

Table 4. Relative intensities of alkyl ions and $[C_3H_5O]^+$ formed by γ-cleavage$_2$

Alkanal	Alkyl ion	Intensity (%)	Ion containing oxygen	Intensity (%)
Butyraldehyde (n-C_4)	CH_3	—	C_3H_5O	5.4
N-valeraldehyde (n-C_5)	C_2H_5	7.3	C_3H_5O	7.1
Caproaldehyde (n-C_6)	C_3H_7	7.2	C_3H_5O	8.0
Enanthaldehyde (n-C_7)	C_4H_9	1.1	C_3H_5O	5.4

5. *δ-cleavage*

The mass spectra of the high n-alkanals show an ion current at $m/e = 71$, corresponding to the formation of $[C_4H_7O]^+$ following a δ-cleavage reaction. The relative intensities of the ions formed by this reaction are given in Table 5.

Table 5. Relative intensities of alkyl ions and $[C_4H_7O]^+$ formed by δ-cleavage.

Alkanal	Alkyl ion	Intensity (%)	Ion containing oxygen	Intensity (%)
N-valeraldehyde (n-C_5)	CH_3	—	C_4H_7O	0.6
Caproaldehyde (n-C_6)	C_2H_5	3.3	C_4H_7O	1.6
Enanthaldehyde (n-C_7)	C_3H_7	9.2	C_4H_7O	2.5

Table 6. Relative intensities of $[M\text{-}H_2O]^+$ ions.

Alkanal	$[M\text{-}H_2O]^+$	Intensity (%)
Propionaldehyde (n-C_3)	C_3H_4	0.5
Butyraldehyde (n-C_4)	C_4H_6	0.4
N-valeraldehyde (n-C_5)	C_5H_8	0.2
Caproaldehyde (n-C_6)	C_6H_{10}	3.8
Enanthaldehyde (n-C_7)	C_7H_{12}	2.6

6. *Formation of $[M\text{-}H_2O]^+$ ions*

The measurements of water peaks formed in the mass spectra of organic molecules upon electron impact [9] give an idea about the fragmentation route for the loss of water from these molecules.

Gilpin and McLafferty [1] observed a peak due to the loss of H_2O in the spectra of n-alkanals. However, this peak was more pronounced in aldehydes containing six carbon atoms and more. This is in agreement with the results of our spectra as shown in Table 6.

7. *Formation of $[M\text{-}C_2H_4]^+$ ions*

The n-alkanals under study show significant peaks corresponding to the formation of $[M\text{-}C_2H_4]^+$ ions which agree with earlier results of Gilpin and McLafferty [1]. The most pronounced peak of this type of ions is that in butyraldehyde which is formed via a β-cleavage with rearrangement (see Table 7).

Table 7. Relative intensities of $[M\text{-}C_2H_4]^+$ ions.

Alkanal	$[M\text{-}C_2H_4]^+$	Intensity (%)
Propionaldehyde (n-C_3)	CH_2O	2.6
Butyraldehyde (n-C_4)	C_2H_4O	27.0
N-valeraldehyde (n-C_5)	C_3H_6O	16.3
Caproaldehyde (n-C_6)	C_4H_8O	6.7
Enanthaldehyde (n-C_7)	$C_5H_{10}O$	2.8

II. Ionization potentials of *n*-alkanals

The ionization potentials of the molecular ions of the various *n*-alkanals were determined using the EDD-method (electron distribution difference technique). Following the method of Winters et al. [5], a computer programme was developed in which the data points were fitted to straight lines using a least squares analysis. The data were first smoothed using the so called moving average method [10] in order to minimize fluctuational errors.

The ionization efficiency (IE) curves for the molecular ion of acetaldehyde is shown in Figure 2. The first arrow in the curve corresponds to the first ionization potential of the molecular ion. The other arrows indicate breaks in the ionization efficiency curve and presumably correspond to the higher ionization potentials. Similar curves were obtained for propionaldehyde, butyraldehyde and *n*-valeraldehyde. However, for caproaldehyde and enanthaldehyde the (IE) curves involved large experimental errors caused by the instability of the molecular ions of these compounds under electron impact. Therefore the ionization potentials for these compounds could not be determined with confidence.

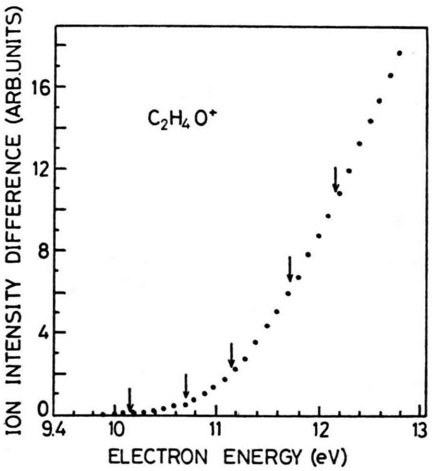

Fig. 2. IE curve for acetaldehyde.

Our results for the ionization potentials together with those available in literature [11] from various techniques are given in Table 8.

Table 8. Ionization potentials of *n*-alkanals in eV.

n-alkanals molecular ion	This work (EDD-Method)	Previous work [11]
Acetaldehyde C_2H_4O	10.14 ± 0.02	10.21 ± 0.01 (PI) 10.21 (RPD)
Propionaldehyde C_3H_6O	9.82 ± 0.14	9.98 ± 0.01 (PI) 10.14 ± 0.10 (EVD)
Butyraldehyde C_4H_8O	9.73 ± 0.15	9.86 ± 0.02 (PI)
N-valeraldehyde $C_5H_{10}O$	9.89 ± 0.12	9.82 ± 0.05 (PI)

PI: Photoionization; RPD: Retarding potential difference; EVD: Extrapolated voltage difference.

Acknowledgement

We gratefully acknowledge the continuous support and interest of Professor Dr. M. El-Nadi during this work.

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